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METHYLENE BLUE DYE ADSORPTION STUDIES OF NOVEL IONIC LIQUID BASED OMMT NANOCOMPOSITE HYDROGELS

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ABSTRACT

A series poly (Acrylamide -co-2-acrylamido-2-methyl-1- propane sulfonate-Ionic Liquid)/OMMT and MMT Nanocomposites (NC) were prepared using ammonium persulfate (APS) as an initiator and N,N′-methylenebisacrylamide(MBA) as the cross-linker. The nanocomposite hydrogels were prepared via in situ polymerization using OMMT and MMT nano clay. The synthesized nanocomposites were characterized by FT-IR, SEM, XRD and TGA techniques. The parameters of swelling and diffusion in water and dye solution were calculated. It was observed that poly (AM-co-AMPS-IL)MMT have higher adsorption than poly (AM-co-AMPS-IL)OMMT and poly (AM-co-AMPS-IL) alone. The hydrogel nanocomposites showed up to 99.7% removal efficiency towards methylene blue dye adsorption study.

KEY WORDS : Ionic Liquid, Swelling behaviour, Dye adsorption study, SEM analysis, Nanocomposite hydrogel, Methylene blue

INTRODUCTION

Dyes and pigments are generally utilized as a part of the leather and textile dyeing, food technology, pharmaceutical, and cosmetic industries (Kiani *et al*., 2011 and Liu *et al*., 2011). It is accounted for that more than 100,000 different commercial dyes and pigments exist, and every year more than 7 x 10^5 tons of dyestuffs are created. Arrival of the dyes to the environment have excited genuine concerns everywhere through the world for the toxic effects of dyeing effluents, for example, mutagenic and carcinogenic activity to aquatic biota and people (Anbia *et al*., 2011 and Nethaji *et al*., 2010). Methylene blue (MB) is a cationic thiazine dye with a chemical name of tetramethylthionine chloride. Broadly utilized as dye in textile industry, MB is effortlessly being perceived because of its appearance as deep blue (at its oxidized state) with a maximum absorption at 609 and 664 nm (Oz *et al*., 2009). On in opposition to its advantages, this stable compound is exceptionally harmful and nearly non-biodegradable which lasts for many years. MB contaminates nature as well as drains the oxygen content and inhibits sunlight from reaching the water source (Sajab *et al*., 2011). In this manner, removing the dyes from wastewater to a satisfactory level before releasing into the natural environment is a challenge for industries. There are numerous investigations on physicochemical/biological strategies of treating colorful effluents, such as oxidation, coagulation/flocculation, electrochemical treatment, ultra filtration, aerobic/anaerobic method, and adsorption/biosorption. Generation of secondary sludge, high capital and operational cost, sensitive operating conditions, and low effectiveness are a few restrictions of the greater part of these treatment methods (Rao *et al*., 2010). As of late, dye removal using functional polymers turn out to be new approach for environmental applications.

Distinctive polymeric adsorbents specifically hydrogels with various functional groups with ability to complex with dyes increased numerous considerations and further investigated (Jeon *et al*., 2008). In general, hydrogel is three-dimensional networks of hydrophilic polymer chains with intermediate properties between liquids and solids (Sahera *et al*., 2013). But, these absorbents basically don't have enough strength. Introducing of nano-clays into hydrogel compositions can be considered as one of the techniques to enhance this property of absorbents (Haraguchi , 2007). It has been accounted for that inclusion of nano-clays in the superabsorbent composition their quality can enhance as well as the rate and dye adsorption capacity will be increased (Liu and Zhang, 2007). We reported swelling behavior of poly (N-cyclohexylacrylamide-co-acrylamide/AMPS- Ionic Liquid) hydrogel (Anbarasan *et al.,* 2013)**.** In this study we prepared two nanocomposite hydrogels by using Acrylamide (AM), 2-acrylamido-2-methyl-1- propane sulfonate-Ionic liquid (AMPS -IL), OMMT and MMT .Also the water swelling and methylene blue adsorption property of these nanocomposite materials was studied.

MATERIALS AND METHODS

Materials

Acrylamide (AM, Merck) was crystallized from acetone/ethanol mixture. Triethylamine (TEA, Aldrich), Ammonium persulphate (APS, Aldrich,) N,N,N',N'-tetra methyl ethylene diamine (TMED, Merck), N, N'-methylene-bis-acrylamide (MBA, Merck), Methylene blue (MB, Merck), Sodium Chloride (NaCl, Merck) and Potassium Chloride (KCl, Merck) , they were analytical reagent grade and used as received without further purification.2-acrylamido-2-methyl-1-propanesulfonicacid (AMPS) was supplied from Aldrich. AMPS-IL was prepared by neutralizing AMPS with TEA in acetone followed by evaporation of the solvent at room temperature. MMT Clay (Merck) was used as received and OMMT was prepared by using a standard procedure.

Preparation of OMMT nanoclay

The crude montmorillonite (2.5 g) was pretreated for 24 h in a 1N NaCl (500 mL) with continuous stirring at 70 °C. Upon centrifugation whitish layer accumulated at the bottom of centrifuge tube as gel. The gel was washed with deionized water to remove chloride ions which resulted Na-montmorillonite. About 8.0 g of sodium montmorillonite was dispersed in water at 80 °C with stirring. 3.1 g of Octadecylammine and 1.2 mL of conc. HCl (35%) were dissolved in hot water with continuous stirring, the dissolution of surfactant occurred. Once got cleared solution and it is transferred to dispersed Na- montmorillonite solution maintained at 80^0C. After 3 h, the Octadecyl montmorillonite (OMMT) was precipitated and washed with hot water to remove impurities (Hoidy *et al*., 2009).

Synthesis of poly (AM-co-AMPS-IL)/OMMT and MMT nanocomposite hydrogel

The optimum molar ratio of initial materials for preparation of poly (AM-co-AMPS-IL) was considered at prior work in our laboratory. Several nanocomposites with different amount of MMT and OMMT were prepared by free radical copolymerization. Typical preparation conditions for samples are as follows: At first AMPS-IL (0.7 g) and 0.050g cross-linker (MBA) was carefully added to the acrylamide (AM) solution (0.3 g). A given amount of MMT or OMMT (0.0, 0.050, 0.100, 0.150 g) kept under ultrasound for 1h before use for getting nano size was slowly added to it. The suspension obtained was mixed 30 min by a 300 rpm magnetic mixer. In the next step, TMED (0.25 mL) and APS (0.050 g) were added to the pore material-polymer mixed solution. The solution containing monomers burged with nitrogen gas for about 30 minutes to remove the dissolved oxygen. Finally, the temperature of the reaction mixture was maintained at 60 °C for 3h. Then the hydrogels were removed from the polymerization tube and dried at 40 °C.

Characterization of Nanocomposite Hydrogels

The surface morphology of the freeze-dried nanocomposites was studied by scanning electron Microscopy. Nanocomposites were performed using Hitach, model-JSM-5000 imaging mode at 30 kV with varying levels of magnification. Fourier transform infrared spectrum (FT-IR) measurements were carried out by using Nicolet Nexus-670 Spectrometer in KBr pellet at room temperature. The X-ray diffraction studies of the nanocomposite hydrogels were carried out using a BRUKER diffractometer (Germany), model D8 Advance, employing rotting Cu anode. The TGA thermo grams were recorded on a PerkinElmer-7 at a heating rate of 10 ^{o}C/min under N_2 protection over a temperature range from room temperature to 800 ^{o}C.

Measurement of properties

Distilled water absorbency

Swelling characteristics were measured by immersing weighed samples of dry Nanocomposite hydrogel and hydrogel in double distilled water and in Methylene blue dye solution. The excess surface water in the swollen gel was removed by blotting and then the swollen gel was weighed. The swollen gel was blotted several times till three consecutive weights are same within limits of experimental error of 1%. All measurements were performed thrice and the reported values are average of at least three individual measurements. The degree of swelling (Ds) most commonly described as swelling ratio is expressed as increase in weight / gm of dried hydrogel after keeping in contact with water for selected period of time (Shih *et al.*, 2008 and Kaith *et al.*, 2010).

$$Ds(\%) = \frac{(W_t - W_d)}{(W_d)} X100 \qquad \text{.... (1)}$$

Here, W_t is the weight of the swollen gel at a given time and W_d is the weight of the dry gel.

Physiological saline solution absorbency

This properties can be evaluated by repeating the measurement method of Ds (%) except varies concentration of NaCl and KCl instead of distilled water.

Removal efficiency (RE %)

A weighed quantity of dry hybrid Nanocomposites with different composition were immersed in enough methylene blue (25 ppm, 20 mL) and kept at 37 ^{o}C. The amount of MB adsorbed was measured spectrophotometrically (λ: 661.6 nm) in periodically taken solution samples and again placed in the same vessel so that the liquid volume was kept constant. Removal efficiency (RE %) of the dye by the Nanocomposites with different composition was calculated by using the following expression:

$$RE(\%) = \frac{(C_o - C)}{(C_o)} X100 \qquad \text{..... (2)}$$

Where C_o and C are the initial and equilibrium concentration of the MB dye solution, respectively (Patel *et al.*, 2009 and Zendehdel *et al.*, 2011).

RESULTS AND DISCUSSION

FT-IR Spectroscopic analysis of Nanocomposite Hydrogel

The Fig.1a and Fig.1b shows FT-IR spectra of Poly (AM-co-AMPS-IL)/OMMT and Poly (AM-co-AMPS-IL)/MMT nanocomposites. In the Fig. 1a, peak 676 cm^{-1} is absorption of the C–Sbond , peak 3393cm^{-1} is absorption of N-H of AMPS-IL as well as AM, peak 1661 cm^{-1} is absorption of C=O of AM and AMPS-IL, peak 1537 cm^{-1} is absorption of $C=ONH_2$ of AM unit. The peak observed at 1488 cm^{-1} corresponding to S=0 (Sym) and 2923 cm^{-1} is due to C-H stretching of polymer backbone. Peak at 2310cm^{-1} indicates coupled OH in-plane bending and C-O stretching. A new peaks at 3517cm^{-1} is due to –OH group between the two planes of the clay and Si-O-Si symmetric stretching mode was observed at 1111 cm^{-1}. Peaks at 597 cm^{-1} and 676 cm^{-}

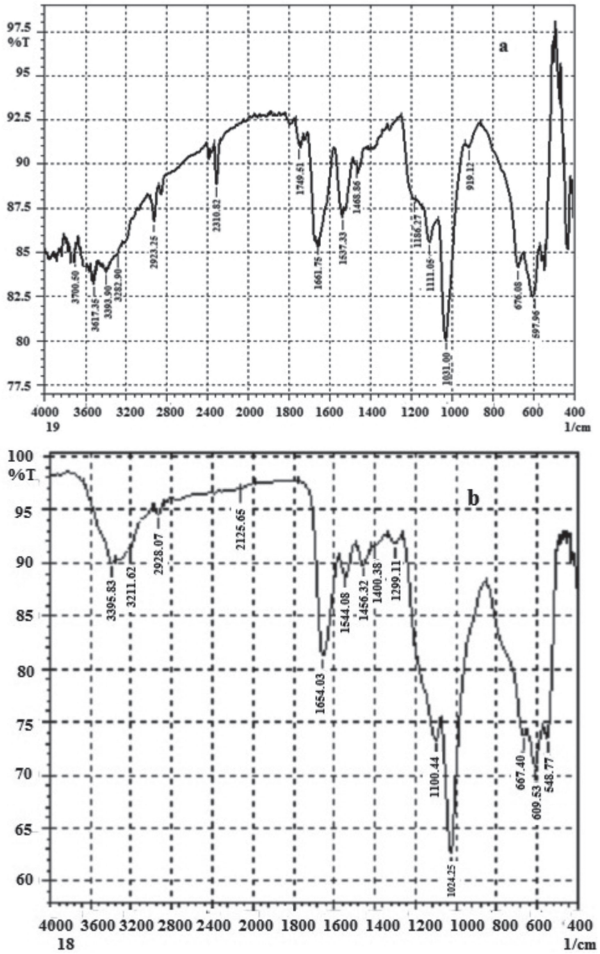

Fig. 1. FT-IR spectra of (a) Poly (AM-co-AMPS-IL)/ OMMT (b) Poly (AM-co-AMPS-IL)/MMT Nanocomposites

^{1} indicates Si-O-Al and R-O-Si (R=A,Mg or Li) respectively.

In the Fig. 1b, peak 667 cm $^{-1}$ is absorption of the C–S bond, peak 3395 cm^{-1}is absorption of N-H of AMPS-IL as well as AM, peak 1654 cm^{-1} is absorption of C=O of AM and AMPS-IL, peak 1544 cm^{-1} is absorption of C=ONH$_2$ of AM unit. The peak observed at 1456 cm^{-1} corresponding to S=0 (Sym) and 2928 cm^{-1} is due to C-H stretching of polymer backbone. Peak a 2125 cm^{-1} indicates coupled OH in-plane bending and C-O stretching. Si-O-Si symmetric stretching mode was observed at 1100 cm^{-1}. Peaks at 609 cm^{-1} and 667 cm^{-1} indicates Si-O-Al and R-O-Si (R=A,Mg or Li) respectively.

Thermogravimetric analysis

The TG-DTA curves of Poly (AM-co-AMPS-IL)/ OMMT and Poly (AM-co-AMPS-IL)/MMT were depicted in Fig. 2. It showed three-step continuous thermal decomposition. The initial weight loss is due to the evaporation of free water and inters layered water present in the sample. The first stage and the second stage is attributed to the thermal decomposition of the amide group of AMPS-IL and the decomposition of crosslinker respectively. The final stage is due to the main chain scission in the polymer back bone. The residual weight percentage indicates the content of nano clay. Nanocomposites showed final decomposition temperature (FDT) at 790 °C. we can conclude that (AM-co-AMPS-IL)/ OMMT and Poly (AM-co-AMPS-IL)/MMT is more thermally stable (Ling and Lu, 2008).

X-ray diffraction analysis

X-ray diffraction patterns of Poly (AM-co-AMPS-IL)/OMMT and MMT clay are shown Fig. 3. Some diffraction peaks at 2θ: 27-63 are clearly seen and can be indexed as the OMMT clay. The wide peak show that the size of the clay is very small, which conforms more amorphous and less crystalline. It showed that the more the amorphous in the matrix more will be the swelling. It was clear that the regular crystal structure of clay was partly destroyed and the clay platelets were intercalated and dispersed in the Nanocomposites (Kaith *et al.*, 2010; Patel *et al*., 2009 and Zhu *et al.*, 2012).

SEM Analysis

The SEM images of Poly (AM-co-AMPS-IL)/ OMMT and Poly (AM-co-AMPS-IL)/OMMT are shown in Fig. 4. The surface morphology of the Nanocomposite was studied by SEM analysis. The

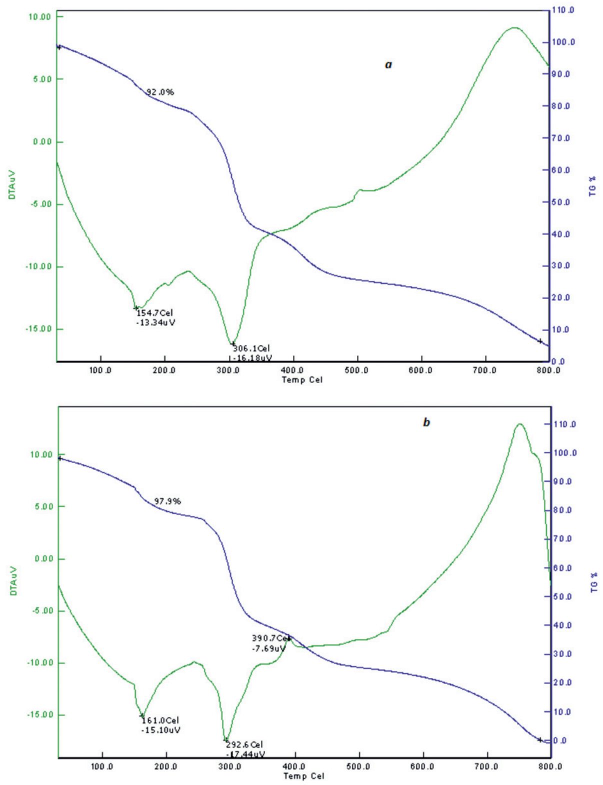

Fig. 2. TGA curves of (a) Poly (AM-co-AMPS-IL)/OMMT (b) Poly(AM-co-AMPS-IL)/MMT

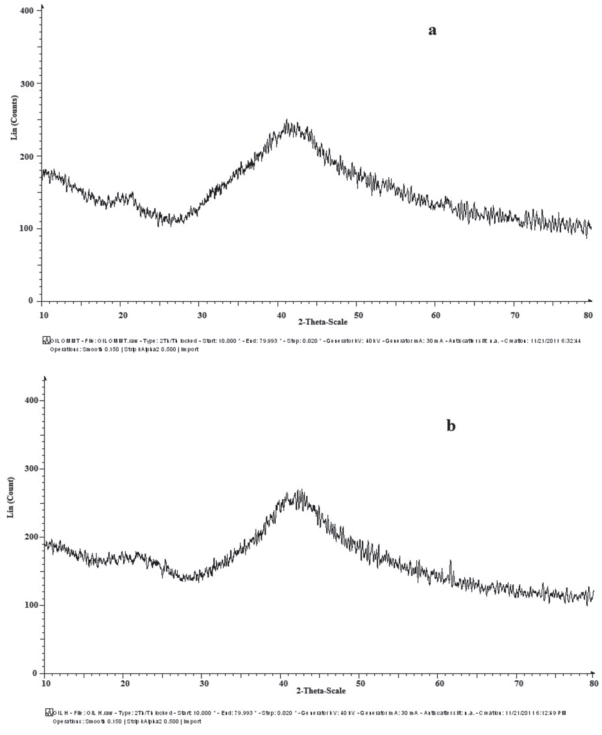

Fig. 3. XRD pattern of (a) Poly (AM-co-AMPS-IL)/ OMMT (b) Poly (AM-co-AMPS-IL)/MMT

SEM micrograph of the composite shows that the diameter of OMMT fibers is in the scale of nm, which confirms the sample of our synthesized hydrogel composite as real composite. It was found that the OMMT clay was dispersed in the polymer network (Yi and Zhang, 2012).

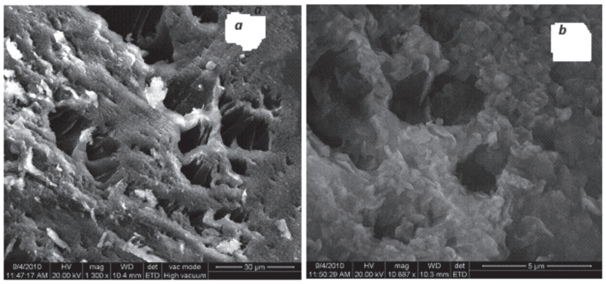

Fig. 4. SEM images of (a)Poly (AM-co-AMPS-IL)/OMMT and (b) Poly (AM-co-AMPS-IL)/MMT

Swelling behavior

The Fig. 5. demonstrates the swelling behavior for poly (AM-co-AMPS-IL), poly (AM-co-AMPS-IL)/ OMMT, poly (AM-co-AMPS-IL)/MMT in water and poly (Am-co-AMPS-IL), poly (AM-co-AMPS-IL)/OMMT, poly (AM-co-AMPS-IL)/MMT with MB at room temperature respectively. It has been observed that incorporation of OMMT and MMT to poly (AM-co-AMPS-IL) increased their swelling ratio. When the poly (AM-co-AMPS-IL) nanocomposites contact with water, water diffuses into it and causes swelling. Equilibrium swelling of the Nanocomposite hydrogels was achieved up to 6 h. When we increase the contact time up to 12 h , we can observed insignificant swelling for all synthesized composite hydrogels. Incorporation of 0.100g clay showed high equilibrium swelling than other. Poly (AM-co-AMPS-IL)/OMMT show higher swelling than poly (AM-co-AMPS-IL)/MMT(Patel *et al.*, 2009 and Zhang *et al.*, 2005).

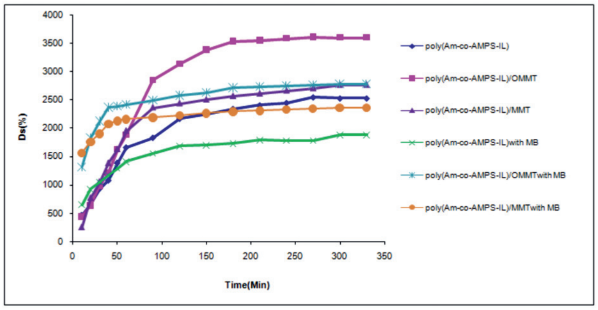

Fig. 5. Curves of swelling ratio vs time for poly(AM-co-AMPS-IL), poly(AM-co-AMPS-IL)/OMMT and poly (AM-co-AMPS-IL)/OMMT nanocomposites

Effect of ionic strength

The Ds (%) of the poly (AM-co-AMPS-IL), poly (AM-co-AMPS-IL)/OMMT and poly (AM-co-AMPS-IL)/MMT nanocomposites have been studied at different concentrations (0.5, 1, 1.5, 2, and 2.5%) of NaCl and KCl are shown in Fig. 6. It was found that Ds (%) decreases with increase in salt concentration. Maximum swelling has been found at 0.5% concentration in all the salt solutions. In water, the composites has maximum osmotic pressure, hence the maximum swelling. But when the composite was placed in NaCl and KCl solutions, the osmotic pressure is lower due to Na^+, K^+ and Cl^- ions (Singh *et al.*, 2007 and Rasool *et al.*, 2008).

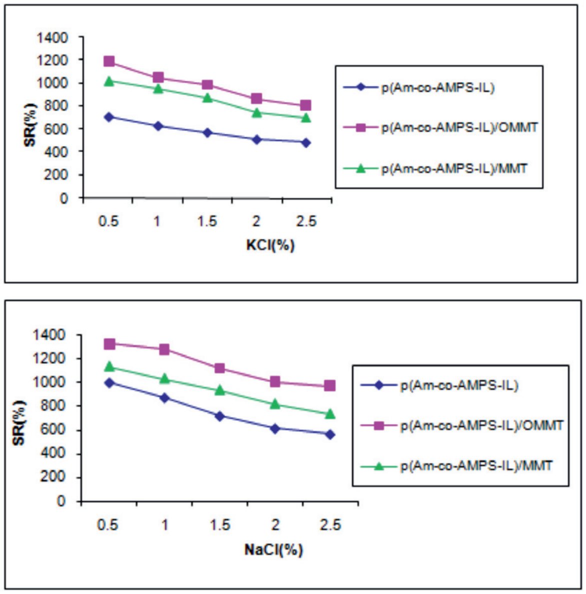

Fig. 6. Effect of electrolyte on swelling of Nanocomposite Hydrogels

Adsorption of Methylene blue

To study the adsorption, a weighed quantity of dry hybrid Hydrogels and Nanocomposites with different composition were placed in aqueous solution of methylene blue for 24 h. After 24 h, all nanocomposites showed dark color compared with the original composites. Also, the color of MB solution became colorless compared with the original solution. Fig. 7a and Fig. 7b shows the removal efficiency of methylene blue poly (AM-co-AMPS-IL)/ OMMT and poly (AM-co-AMPS-IL)/ MMT composites, the maximum adsorption of MB from aqueous solutions about 99.7% and 94.8% by OMMT and MMT respectively. Also, when we used of poly (AM-co-AMPS-IL) alone, the maximum adsorption is about 53.5% only. Removal effect of MB increased when the OMMT and MMT was added to (AM-co-AMPS-IL). The OMMT clay have higher adsorption related to MMT clay. From the Fig. 8, we noticed the percentage of dye adsorption of MB was low when the content of MMT/ OMMT at 0.150mg in the hydrogels (Patel *et al.*, 2009 and Ekici *et al.*, 2006).

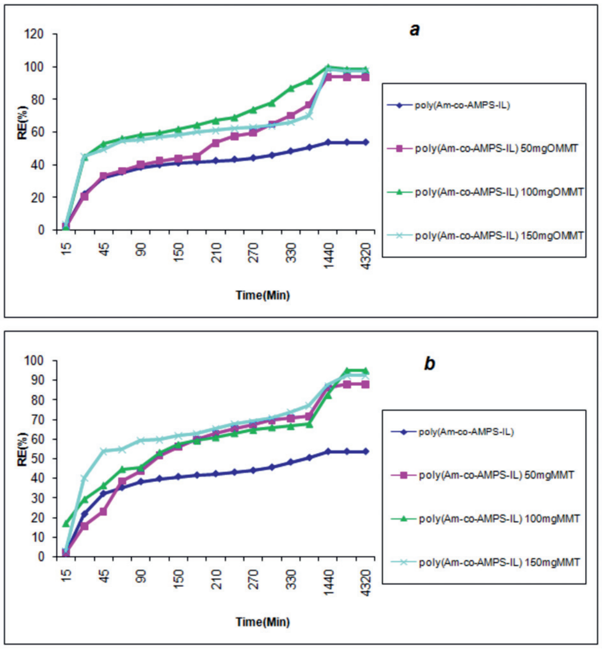

Fig. 7. Effect of addition of OMMT on efficiency of MB removal (a) and effect of the MMT content on efficiency of MB removal (b).

Diffusion studies

The diffusion of water through polymer network is associated with the physical-chemical properties of the Nanocomposite Hydrogels. lnF – lnt curves of poly (AM-co-AMPS-IL), poly (AM-co-AMPS-IL)/ OMMT and poly (AM-co-AMPS-IL)/MMT in MB dye solution are given in Fig. 8. The values of 'n' are shown in Table 1. It can be observed that these results support Fickian mechanism (Ekici *et al.*, 2006). In the Fickian diffusion, the mobility rate for the dye molecules in solution is smaller than the segmental relaxation rate of the polymer chain.

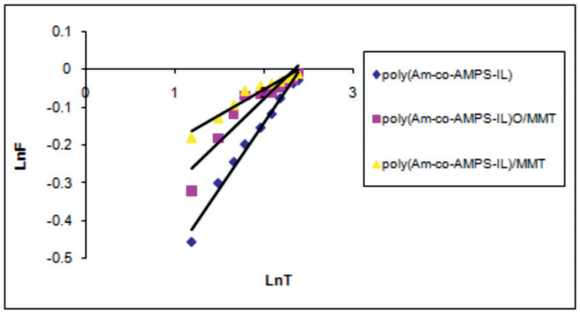

Fig. 8. Diffusion studies of MMT /OMMT Nanocomposite Hydrogels

Table 1. Diffusion parameters of MB loaded Nanocomposite Hydrogels

MB loaded Hydrogels	n	Mechanism
poly (AM-co-AMPS-IL)	**0.34**	Fickian
poly (AM-co-AMPS-IL)/OMMT	**0.22**	Fickian
poly (AM-co-AMPS-IL)/MMT	**0.13**	Fickian

CONCLUSION

In this study, a series of poly (AM-co-AMPS-IL) MMT/OMMT Nanocomposite Hydrogels were synthesized by free radical copolymerization. The SEM analysis showed that clay materials are dispersed on poly (AM-co-AMPS-IL) matrix and XRD showed interaction between Clay particles and poly (AM-co-AMPS-IL). The results indicated the removal of MB from batch experiments showed that the amount of dye uptake increased with increasing of contact time. Removal effect of MB increased with increasing amount of nano clay up to 100 mg of OMMT/MMT content in hydrogel matrix. At higher content of clay in hydrogels the adsorption capacity remains constant. The maximum adsorption of MB 99.7 % achieved on poly (AM-co-AMPS-IL) OMMT. The OMMT clay has greater adsorption capacity than MMT clay. Our synthesized nanocomposite hydrogels may be considered as good adsorption material for dye effluent treatment.

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